Surfactant properties of oxygen in the homoepitaxial growth of Fe: a MDS study

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Abstract

The growth of ultra thin iron films (up to a thickness of 5–6 ML) on O(1×1)–Fe/Ag$(0\,0\,1)$ has been investigated by means of He reflectivity (R_{He}) and metastable de-excitation spectroscopy. The presence of oxygen induces a quasi-ideal layer-by-layer growth at variance with the case of the homoepitaxial growth of iron on Fe$(0\,0\,1)$. The surface electronic density of states suddenly changes upon the deposition of the first half of a monolayer. After the sudden change in the first stages of the growth, the surface density of states of both O$_{2p}$ and Fe$_{3d}$ states remains essentially unchanged, irrespectively of the thickness of the deposited film. This provides a clear indication that oxygen floats at the surface acting as a surfactant for the growth of iron on O(1×1)–Fe/Ag$(0\,0\,1)$. The stationary fraction of oxygen that remains on the topmost layer as growth proceeds depends on the substrate temperature. Post-growth annealing up to 650 K restores the initial coverage of oxygen and the ordered O(1×1) phase. © 2001 Elsevier Science B.V. All rights reserved.

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A great progress has been made in the study of the magnetic properties of low-dimensional systems over the past few years [1]. The strong interest in low-dimensional magnetism of thin films, surfaces and interfaces results from the novel properties of these systems which are of great importance in the design of new magnetic devices.

With regard to surface magnetism, recent experiments have demonstrated the strict correlation between surface magnetic properties and surface morphology [2,3]. An effective method to observe this correlation is to monitor the surface magnetisation during the growth of magnetic films which exhibit a layer-by-layer (LbL) growth. During this kind of growth the defect density of the growing front undergoes cyclic oscillations and, when the above mentioned correlation exists, surface magnetisation exhibits oscillations with a period corresponding to the completion of each monolayer.

If the homoepitaxial growth is of 3D type, as in the case of Fe homoepitaxy on Fe$(0\,0\,1)$ [4], an appealing method to induce a LbL growth is provided by surfactant species [5,6]. In the case of iron homoepitaxial growth, it is known that preadsorption of an O(1×1) phase on Fe$(0\,0\,1)$ promotes a LbL growth with oxygen floating at the surface and acting as a surfactant promoting interlayer Fe transport [7].

In the present paper, we report a study of the influence of the substrate temperature on the

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amount of oxygen floating at the surface after iron deposition on O(1×1)–Fe/Ag$(0\,0\,1)$.

We use metastable de-excitation spectroscopy (MDS) to investigate the surface electronic properties of ultrathin iron films grown on O(1×1)–Fe/Ag$(0\,0\,1)$. MDS exploits the electron emission induced by the de-excitation at the surface of metastable helium atoms. This technique is surface specific as it is sensitive to the electronic states which spill out into the vacuum at a distance of about 2–3 Å from the surface plane [8–10]. Obviously, the surface specificity is particularly suitable for the determination of the density of states of the growing front and therefore to investigate the influence of the substrate temperature on the amount of oxygen on the film surface [11,12]. Quantitative information on the surface density of states are extracted from the experimental energy distribution curves of the emitted electrons by means of the model thoroughly described in a previous paper [13] where the experimental apparatus has been described in detail, too.

The substrate on which iron films are grown has been obtained by evaporating 50 ML of Fe on the $(0\,0\,1)$ surface of a silver single crystal prepared by means of successive cycles of sputtering with Ne$^+$ at 3 keV followed by annealing at 750 K. Fe has been evaporated by electron bombardment of a rod. In order to minimise the amount of silver segregated at the surface, the iron film was deposited on the Ag$(0\,0\,1)$ substrate held at 120 K [14]. The film surface was then exposed to oxygen (7 L; 1 L = 10^{-6} Torr s) and subsequently annealed at 500 K. This procedure produces a well ordered O(1×1) overlayer. The analysis of the He diffraction patterns from the O(1×1)–Fe/Ag$(0\,0\,1)$ and the O(1×1)–Fe$(0\,0\,1)$ phases demonstrates that the long range order is similar in the two cases. The presence of oxygen on top of the Fe film inhibits the segregation of Ag to the surface as it can be deduced by examining the MDS energy distribution curves and comparing them to the ones measured as a function of the annealing temperature for Fe/Ag$(0\,0\,1)$ [15].

The growth of iron on O(1×1)–Fe/Ag$(0\,0\,1)$ was monitored by observing the helium reflectivity (R_{He}) as its strong dependence on the surface defect density provides an effective way to determine the

characteristics of the growth [16]. As in the case of the iron deposition on O(1×1)–Fe$(0\,0\,1)$, also on this substrate R_{He} exhibits strong and regular oscillations during the deposition both at room temperature and at 150°C proving that iron grows in a quasi-ideal LbL mode. R_{He} oscillations during the growth process have been used to determine the deposition rate and the thickness of the grown iron film. After the deposition, annealing at 650 K allows a recovery of the initial conditions both concerning the R_{He} intensity and the MDS energy distribution curve.

Iron has been evaporated at a deposition rate of 0.3 ML/min. Both at room temperature and at 150°C, the surface do not show any detectable change of the structure after the interruption of the deposition. In fact, the real time measurement of R_{He} during the deposition and after its interruption shows that it maintains the intensity reached immediately before the interruption of the deposition.

Surface density of states does not appear to change after deposition has been switched off as confirmed by the fact that the energy distribution curves collected at different time delays from the interruption of the deposition process do not show any detectable variation. Therefore we can conclude that neither the structure nor the density of states of the grown film change during the period required for the MDS measurements.

MDS energy distribution curves have been measured after the deposition of iron films of different thickness on O(1×1)–Fe/Ag$(0\,0\,1)$. At both temperatures (room temperature and 150°C), the MDS energy distribution curves suddenly change after the deposition of the first half of a monolayer but remain essentially unchanged as the deposition goes on. We have tested this behaviour up to a film thickness of about 5–6 ML. The energy distribution curves of the emitted electrons collected from the O(1×1)–Fe/Ag$(0\,0\,1)$ phase and after the deposition of 0.5 ML of iron at room temperature and at 150°C are shown in Fig. 1 (dots).

The experimental energy distribution curves have been fitted by using the model previously reported [13] and the densities of states corresponding to the calculated curves (continuous lines in Fig. 1) are reported in Fig. 2. The peak in the
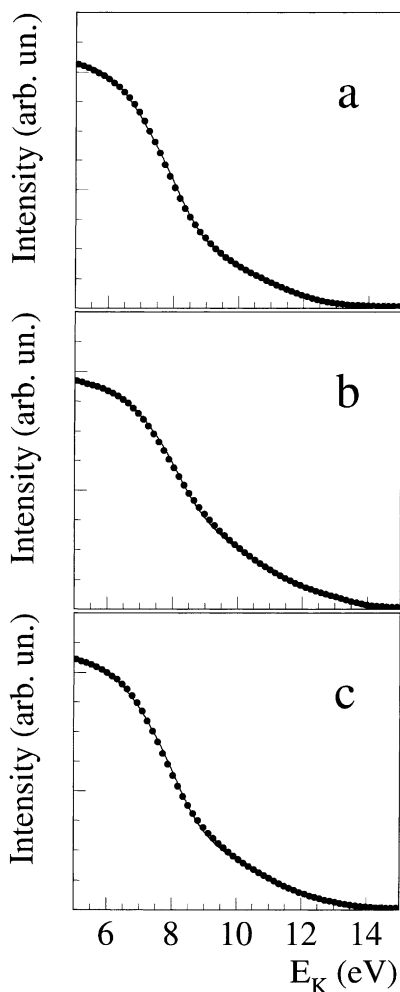
Fig. 1. Energy distribution curves for O(1×1)–Fe/Ag$(0\,0\,1)$ (panel a) and after the deposition of 0.5 ML of Fe on the substrate held at room temperature (panel b) and at 150°C (panel c). The experimental data are represented by dots while the continuous lines provide the fit to the data (see text).

Fig. 2. Density of states obtained by fitting the experimental data relative to the O(1×1)–Fe/Ag$(0\,0\,1)$ (panel a) and after Fe deposition at room temperature (panel b) and 150°C (panel c).

density of states at $E_B \simeq 6$ eV is due to O$_{2p}$ states, while the shoulder at low binding energies can be ascribed to Fe$_{3d}$ states [17]. A comparison with the "reference" O(1×1)–Fe/Ag$(0\,0\,1)$ data (panel *a* of Fig. 2) shows that, upon iron deposition, the contribution of O$_{2p}$ states decreases, while there is a contemporary increase of the iron states. In Fig. 2, even if in arbitrary units, the scales of the $n(E)$ axes are the same for all the panels and the intensities of all peaks can be directly compared. The above mentioned decrease of the contribution of
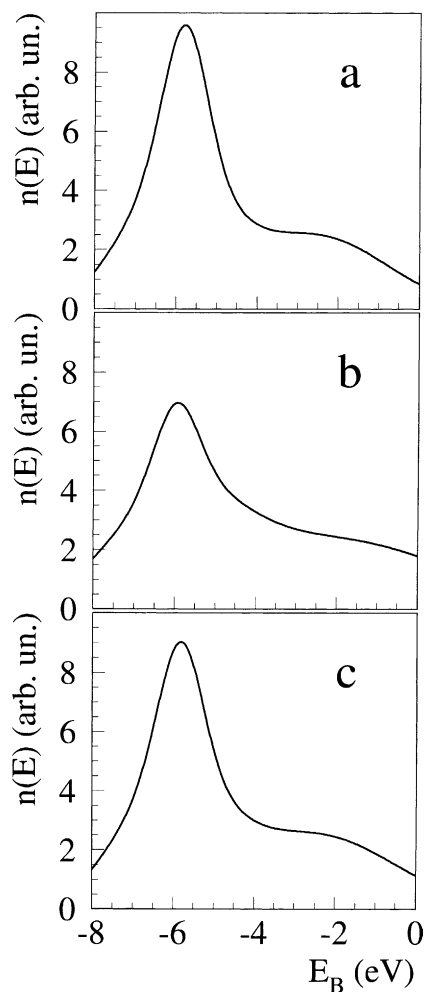
O$_{2p}$ states is strongly influenced by the substrate temperature. It can be estimated as 30% for the growth at room temperature and 5% in the case of the growth at 150°C. The corresponding increase of the Fe states evaluated at $E_B \simeq 0.8$ eV (the binding energy of Fe$_{3d}$ states) is of comparable magnitude.

In all the densities of states obtained by fitting the energy distribution curves measured after the deposition of iron films of different thickness only the structures ascribed to oxygen and iron states can be detected. Moreover, apart from the relative

intensities of the O_{2p} and Fe_{3d} states, they are substantially equivalent to the density of states of the $O(1 \times 1)$–Fe/Ag(0 0 1) phase.

The changes of the density of states upon Fe deposition could be attributed to the modification of the order at the surface and in particular to the occurrence of growth-induced defects in the $O(1 \times 1)$ phase [18,19]. Nevertheless, the strong oscillations of R_{He} observed during the growth of the iron film indicates that the defect density at the surface is substantially different when a half integer or an integer number of layers has been deposited. The fact that there is no further detectable variation of the energy distribution curves and therefore of the surface density of states after the deposition of the first half of a monolayer indicates that such influence of the order is not predominant. Moreover, a study of the surface structure performed during the growth of iron on $O(1 \times 1)$–Fe(0 0 1) performed by means of He diffraction measurements, indicates that the floating oxygen maintains an ordered (1×1) structure [7]. As a consequence, we ascribe the changes of the density of states observed in the first stages of growth to a change of the surface composition. The decrease of the O_{2p} states and the contemporary increase of the Fe_{3d} states can be therefore related to an actual decrease of the number of oxygen atoms on the surface. Since an annealing up to 650 K after the iron deposition restores the initial conditions of the surface and therefore the initial oxygen coverage, we can conclude that the "lost" oxygen atoms do not desorb during the deposition but instead get buried subsurface.

In summary, we have investigated the growth of ultra thin iron films on $O(1 \times 1)$–Fe/Ag(0 0 1) by means of He reflectivity and metastable deexcitation spectroscopy. We find that oxygen acts as a surfactant in the growth of iron on $O(1 \times 1)$–Fe/Ag(0 0 1) promoting a LbL growth. The extreme surface sensitivity of MDS has been used to determine the oxygen coverage after the deposition. We find that a fraction of the oxygen atoms of the $O(1 \times 1)$ phase adsorbed on the substrate floats on the growing front during the deposition. The fact that oxygen atoms float during the deposition guarantees that the surfactant induced LbL growth is still effective after deposition of at least 5–6 ML. The "lost" oxygen atoms get buried subsurface in the initial stages of the growth and the fraction of buried oxygen atoms depends strongly on the substrate temperature during the deposition.

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